

Application of Fourier Transform Infrared Emission Spectrometry to Surface Analysis



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Abstract:

Infrared emission spectra of thin polymer layers on flat aluminum plate have been measured using Fourier transform infrared spectrometry. The detection limit of Fourier transform infrared emission spectrometry (FT-IR-EMS) was found to be comparable with that of Fourier transform infrared reflection absorption spectrometry (FT-IR-RAS) when an emission ray was collected at a viewing angle of 70°. The merits of FT-IR-EMS over FT-IR-RAS were demonstrated in the measurement of nonflat surfaces. The residual lubricant on steel tire cords could be detected efficiently by the FT-IR-EMS mode. The linear relationship found between the relative emission intensity and the thickness of film represents the possibility for a quantitative analysis of a thin overlayer on metal surface.

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0.922 μm , facilitating sulphur analysis simultaneously with that of other elements of interest.

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Application of Fourier Transform Infrared Emission Spectrometry to Surface Analysis

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Infrared emission spectra of thin polymer layers on flat aluminum plate have been measured using Fourier transform infrared spectrometry. The detection limit of Fourier transform infrared emission spectrometry (FT-IR-EMS) was found to be comparable with that of Fourier transform infrared reflection absorption spectrometry (FT-IR-RAS) when an emission ray was collected at a viewing angle of 70° . The merits of FT-IR-EMS over FT-IR-RAS were demonstrated in the measurement of nonflat surfaces. The residual lubricant on steel tire cords could be detected efficiently by the FT-IR-EMS mode. The linear relationship found between the relative emission intensity and the thickness of film represents the possibility for a quantitative analysis of a thin overlayer on metal surface.

Index Headings: Infrared emission spectrum; Fourier transform infrared spectroscopy; Surface analysis.

INTRODUCTION

Fourier transform infrared spectrometry (FT-IR), with its high sensitivity, allows for the detection of a thin layer on metal surface. We have previously presented the application of FT-IR to the measurements of the mono-molecular layer of cadmium arachidate on glass with the FT-IR-ATR mode¹ and also of the oxide layer on a copper plate with the infrared reflection absorption spectrometry (FT-IR-RAS) mode.² The infrared emission spectrometry (FT-IR-EMS) is another choice of measurement mode for studying vibration spectra of surface species.

The interferometer was utilized for the emission measurement of weak infrared radiation from a wide variety of materials such as minerals and rock specimens in the early stage of the development.³ The first attempt to apply FT-IR-EMS to surface analysis was made by Low and Coleman. They observed the emission spectrum of oleic acid on aluminum foil.⁴ Griffiths measured the emission spectra of thick and thin films of silicone grease on aluminum sheets and found that the characteristic bands of silicone could be seen in the thin film whereas they were smeared out by the reabsorption⁵ in the thick film. The emission technique coupled with FT-IR was also used to study absorbed species in a catalytic process.⁶ A problem in extending the emission technique to surface analysis is the strong background emission which superimposes on a weak emission from surface.⁷ Durana improved the technique by cooling the spectrometer and sample chamber in order to decrease the competing background emission and also the spectral noise.⁸ She could obtain the spectrum of polymethylmethacrylate of 38-Å thickness on an evaporated gold film, although the method requires too much elaboration from practical point of view.⁹ Recently Greenler calculated the angular distribution of the intensity of the emission from molecules adsorbed on metal surface. He concluded that the coherent emission from an oscillator dipole normal to a metal surface showed the intensity maximum when the viewing angle is between 70° and 80° from the normal. On the other hand the emission intensity in the direction normal to the surface is approxi-

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Optical Diagram of FT-IR-EMS

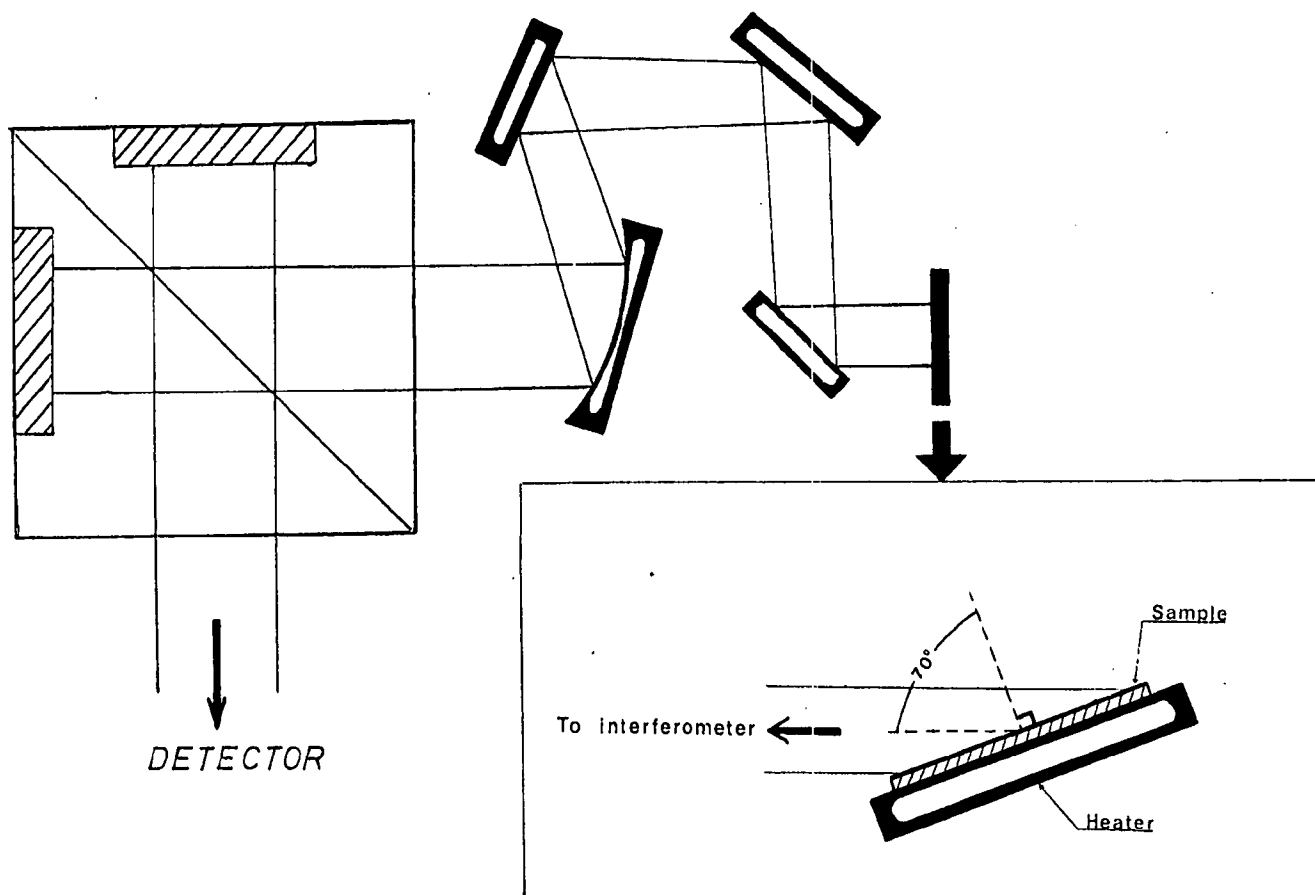


FIG. 1. The optical alignment of the sample emitter in FT-IR-EMS.

mately zero because of the destructive interference between the light coming directly from adsorbed molecules and the reflected light from the interface to the metal substrate.¹⁰ Suetaka succeeded in obtaining the emission spectrum of polyvinylacetate and also aluminum oxide on aluminum at a viewing angle of 80° by applying the polarization modulation technique to IR-EMS.¹¹

In this paper, we describe the results of emission spectra obtained in our laboratory using a viewing angle of 70°. We first have checked the surface sensitivity of the technique with poly-acrylonitrile co-styrene thin films on aluminum. We also have extended the emission technique to rough metal surfaces, such as steel tire cords and copper wires. The adhesion of the brass-plated steel tire cord to rubber is one of the important properties of steel belted radial tires.¹² The effect of the presence of residual drawing lubricant on the cords on the adhesion behavior has not been investigated with IR spectrometry before the present work. We will discuss the potentiality of this technique to nonflat surfaces making use of the example of the steel tire cords.

EXPERIMENTAL

Spectrometer. Digilab Model FTS-20B/D with a special attachment described later was used in our experi-

ments. Typically 800 to 1000 scans were accumulated at the resolution of 8 cm⁻¹. The TGS (triglycine sulfate detector) was replaced by MCT (mercury cadmium telluride detector) because the latter was found to give an improved signal-to-noise ratio in the emission mode. Infrared reflection absorption spectra were obtained with the FT-IR-RAS attachment described in the previous paper² to compare with the emission spectra.

Sample Preparation. An aluminum plate of 50 × 30 mm size was polished to a mirror finish with a metal polish (PIKAL), cleaned with a soap solution, washed in an ultrasonic cleaning bath with a detergent, acetone, n-hexane, and chloroform, successively. Then the plate was dipped into a chloroform solution of poly-acrylonitrile co-styrene (PAS) and drawn out with a constant velocity to coat a thin polymer film. The resultant thickness of polymer films controlled by both the polymer concentration and the drawing velocity was determined by uv light absorbance at 260 nm of chloroform solution prepared from the film of the measured area. Copper wire, 2 mm in diameter, was cut 30 mm in length and also coated by PAS film in a way similar to that described above for the aluminum plate.

Brass-plated steel tire cords (5 × 0.3) were also cut into 30 mm lengths and washed with acetone in the ultrasonic bath. A small amount of the lubricant which

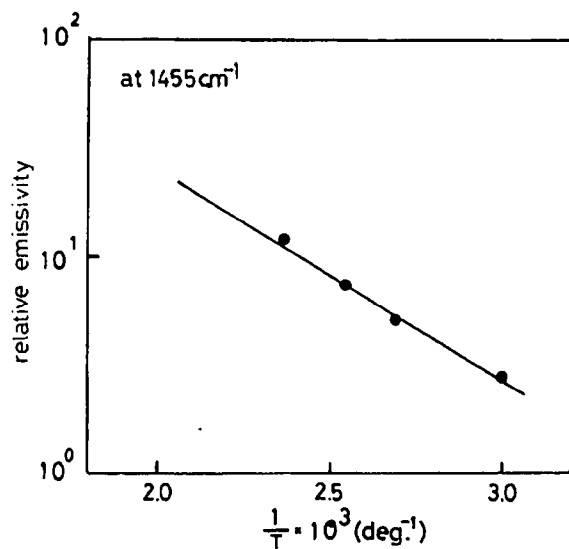


FIG. 2. Dependence of emission intensity on the sample temperature.

contained 0.1 g of organic solutes and 0.11 mg of ammonium phosphate in 1 mL of aqueous solution was applied on the tire cord. The average thickness of the lubricant layer was estimated from the surface area of the cords and a volume of the used lubricant.

The infrared light source was replaced with a sample with heating equipment in the emission experiment as indicated in Fig. 1. A variable temperature cell holder produced by Hitachi Ltd. was used with slight modification within the temperature range between 80 and 190°C with accuracy of $\pm 1^\circ\text{C}$.

Sample Heating Stage. The sample holder was tilted and fixed at a viewing angle of 70° for a flat sample to get a high signal-to-noise ratio according to Greenler's calculation (see Fig. 1). Nonflat samples such as tire cords and wires were mounted on a copper block and put into the holder in the usual vertical position.

Ratio Spectra. In our experiment a single beam spectrum of the sample is ratioed against one of the emission from the substrate to obtain a spectrum of a thin layer on metal. When attempting to obtain the weak emission spectrum, the emission from the beamsplitter which constitutes a substantial fraction of the background signal has to be subtracted from both the sample and the substrate single beam spectra before being ratioed. Thus the emittance, ϵ , is defined as

$$\epsilon = \frac{I_s - I_b}{I_R - I_b}$$

where I_s denotes the intensity of a single beam emission from the sample, I_R denotes that from the reference substrate, and I_b denotes the intensity of the background emission from the beamsplitter.

RESULTS AND DISCUSSION

In order to confirm that the emission measured is really coming from the heated samples, the dependence of emissivity on the sample temperature was checked. The 1455 cm^{-1} band from PAS of $3000\text{-}\text{\AA}$ thickness on

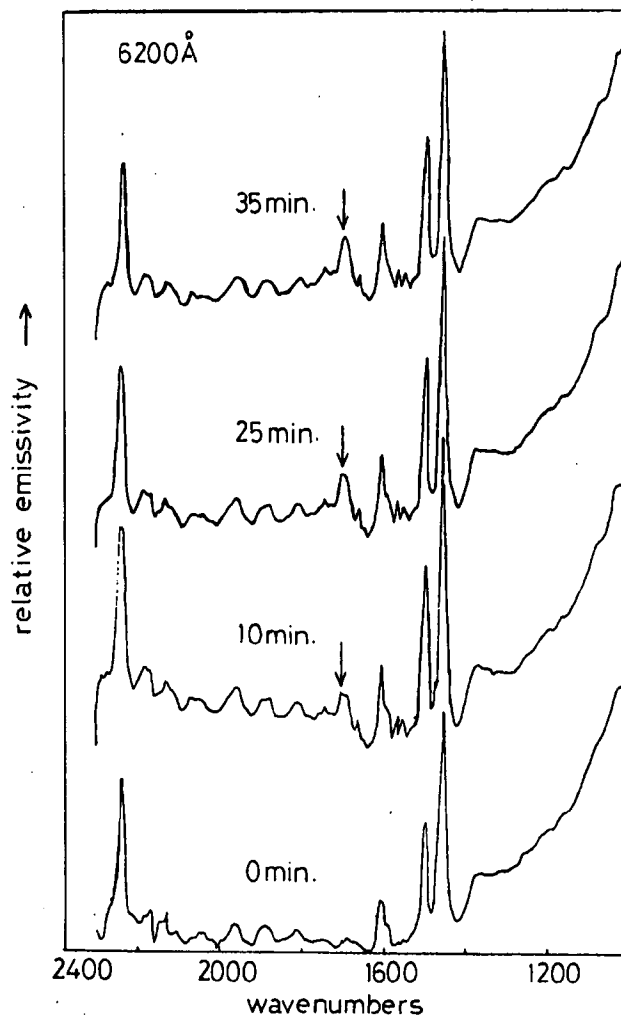


FIG. 3. Thermal decomposition of a sample (PAS) in high temperature measurement.

aluminum foil was used for the purpose. The linear dependence of the exponential of emissivity on the inverse of temperature shown in Fig. 2 indicates clearly that emission intensity is proportional to the population of the vibrationally excited state determined by the Boltzmann distribution law, thus guaranteeing authenticity of the experiment.

Higher temperature is desirable for the better signal-to-background ratio in the emission spectroscopy. Figure 3 shows an example of high temperature measurement of PAS of $3000\text{-}\text{\AA}$ thickness on aluminum foil at 190°C . Spectra of considerably good quality could be obtained at this temperature. However, a band at 1690 cm^{-1} grows with duration of time. It is safely assigned as the stretching band of acetophenone type carbonyl formed by thermal oxidation.¹³ This indicates that the emission measurement should be done at lower than 150°C for most of the organic polymers.

In order to examine the surface sensitivity of FT-IR-EMS, thin films of PAS of different thickness on the aluminum foil were measured as indicated in Fig. 4. The characteristic bands of PAS at 700 , 760 , 1450 , and 1500 cm^{-1} are clearly observed even in the thinnest film of

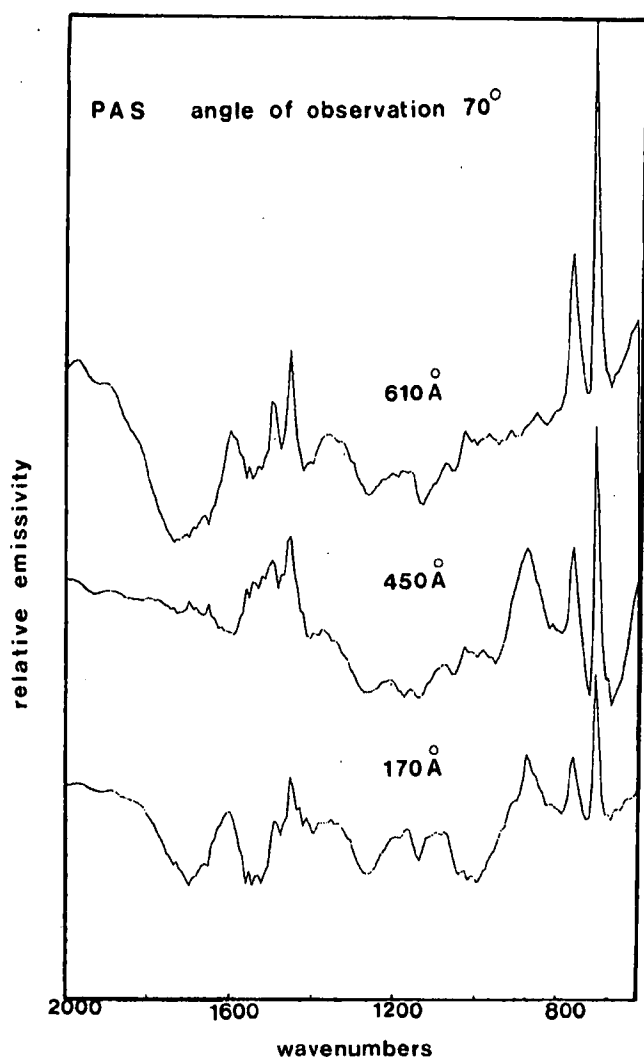


FIG. 4. Emission spectra of thin films of PAS.

170-Å thickness. There is interference at 875 cm^{-1} due to the emission from GeO_2 on the surface of the beam-splitter. It is difficult to subtract this band completely out because the beamsplitter is kept at 40°C in order to prevent water vapor deposition, and its temperature more or less fluctuates. The graphical representation of the relative emission intensity of the 700 cm^{-1} band of PAS as a function of the film thickness is given in Fig. 5. The linear relationship suggests that the fraction of the emission energy absorbed in the path of polymer film is negligibly small under 1000 Å , although there is tendency for saturation of intensity due to reabsorption over 1500 Å . From the observation it can be safely concluded that IR spectrum of down to 100 Å PAS film can be measured with the FT-IR-EMS mode with the viewing angle of 70° . The detection limit here is comparable with that of RAS described in the previous paper.²

FT-IR-EMS and FT-IR-RAS are more or less competing techniques as methods for thin layer analysis on metals because, as established above, the surface sensitivities are in a comparable range. Advantage of EMS over RAS is expected in nonflat samples. There is considerable decrease in reflecting light intensity and also

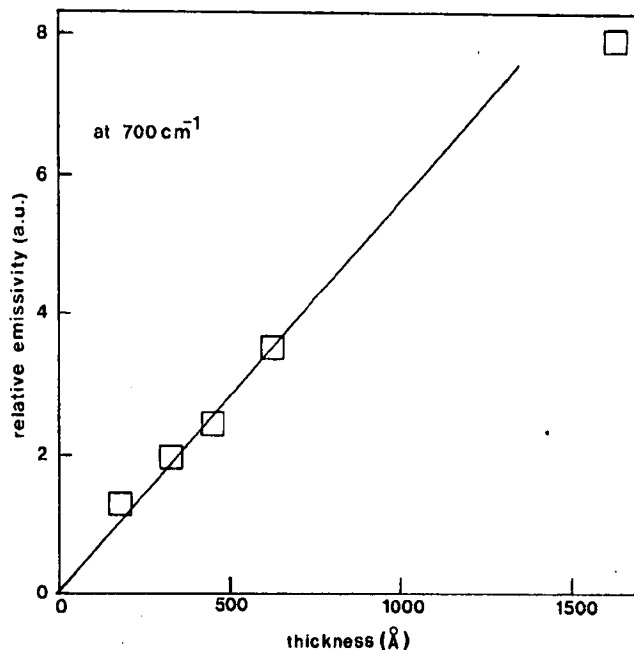


FIG. 5. Dependence of emission intensity on thickness of the thin polymer films on aluminum.

lack of a well-defined angle of reflection in rough or non-flat surfaced samples. These conditions are unfavorable for RAS, whereas there is no such rigid restriction for EMS.

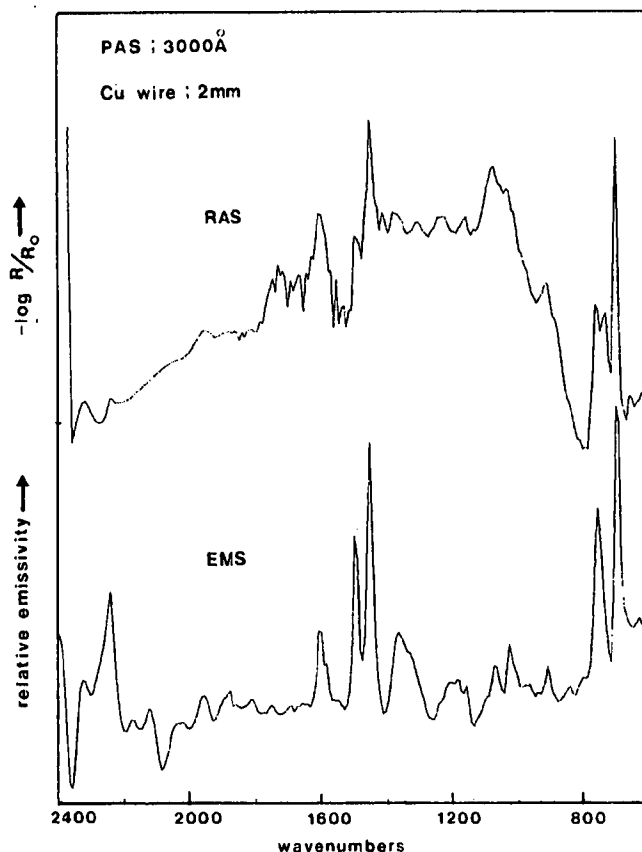


FIG. 6. Comparison between FT-IR-EMS and FT-IR-RAS for a thin polymer film coated on copper wires.

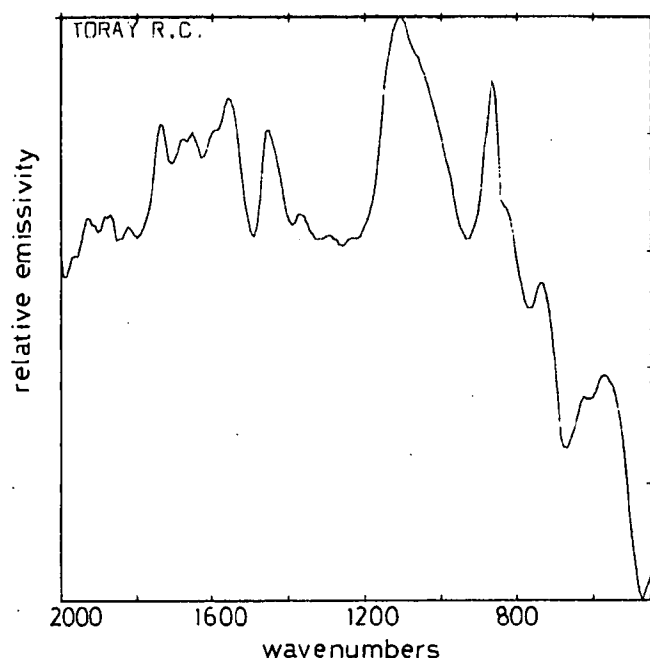


FIG. 7. An FT-IR-EMS spectrum of the thin lubricant film on steel tire cord surface.

Comparison between the two modes of measurement on exactly the same nonflat sample, PAS of 3000-Å thickness on the copper wires of 2-μm diameter, is shown in Fig. 6. The improved signal-to-noise ratio and the better background flatness of EMS compared with PAS are obviously observed in the spectra.

As an example of real samples to be analyzed effectively by FT-IR-EMS, measurement of a lubricant on brass-plated steel tire cords was tried. Influence of the residual lubricant on the steel tire cords on adhesion to rubber has become a center of interest, after the effects of elemental composition and oxidation states of copper and zinc on brass surface were well understood.

An example of the measured spectra is shown in Fig. 7 for a sample of the lubricant with thickness of 1800 Å. The quality of the spectrum is reasonably good for a thin film of irregular shape and it also agrees well with the transmission absorption spectrum of a liquid film of the same sample on KRS-5 plate. The observed bands are summarized and assigned in Table I. The lubricant seems to have hydrocarbon, ester, amide, carboxylate, ammonium ion, and phosphate ion from the identified functional groups. It agrees well with frequently used

TABLE I. Assignment of the observed emission bands from the lubricant on the steel tire cords.

Frequency	Assignment
1735 cm ⁻¹	ν C=O
1650 cm ⁻¹	amide 1
1550 cm ⁻¹	amide 2, ν COO ⁻
1455 cm ⁻¹	δ CH ₂
1400 cm ⁻¹	ν NH ₄ ⁺ , ν COO ⁻
1370 cm ⁻¹	δ CH ₃
1250 cm ⁻¹	ν C-O
1105-1125 cm ⁻¹	ν_3 (PO ₄ ³⁻)

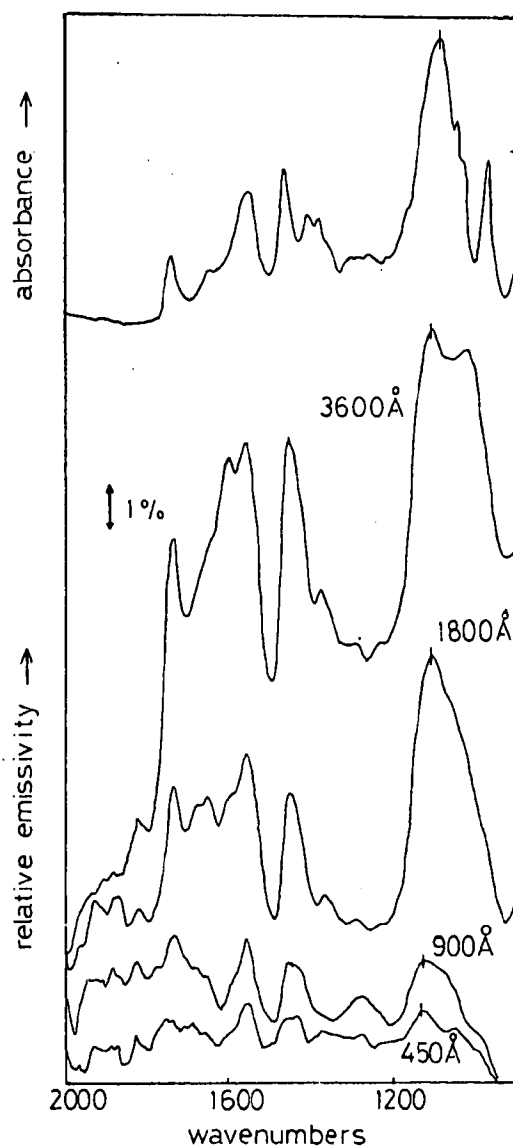


FIG. 8. FT-IR-EMS spectra of the lubricant of various thickness on steel tire cords compared with a transmission absorption spectrum of the same sample on a KRS plate.

composition of a lubricant. The carboxylate observed is considered to be generated from a carboxylic acid in the lubricant by reaction with brass surface. The band of phosphate ion shifts from 1090 cm⁻¹ in the absorption spectrum to 1120 cm⁻¹ in the emission spectrum. The shift may be interpreted again by the interaction of phosphate ion with brass surface.

The emission spectrum has an intense band of GeO₂ at 890 cm⁻¹ due to the beamsplitter, although the subtraction in the single beam spectra is done as described before. We have also tried subtraction in the interferogram stage as suggested by Kember,¹⁴ but GeO₂ emission was not eliminated efficiently.

The emission spectra of the lubricant with varying thickness are shown in Fig. 8 together with a transmission absorption spectrum of a liquid film on a KRS plate. Plotting of emissivity of the 1455 cm⁻¹ band against the thickness in Fig. 9 reveals a linear relationship. This

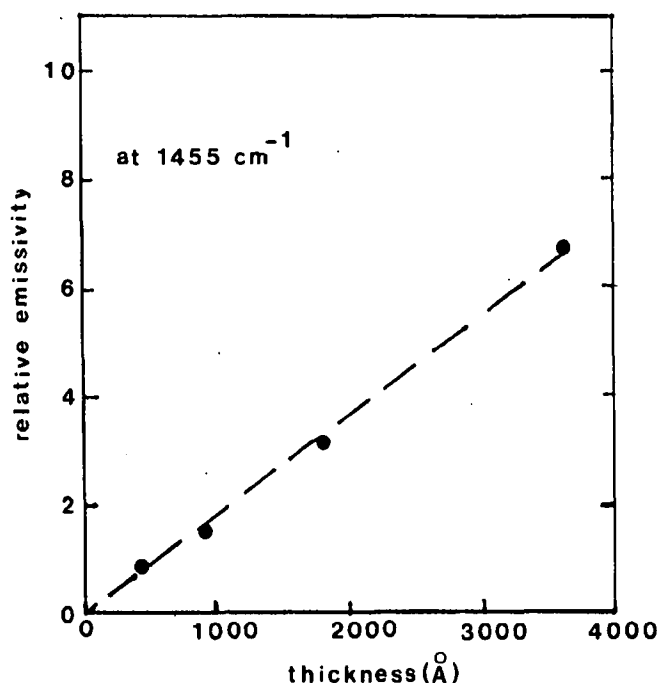


FIG. 9. Dependence of emissivity of 1455 cm^{-1} band of the lubricant on the film thickness.

indicates potentiality of the technique for the semi-quantitative analysis.

CONCLUSION

This study has shown that FT-IR-EMS had surface sensitivity good enough for detecting ca. $100\text{-}\text{\AA}$ thick polymer thin films on metals. It is comparable to FT-IR-RAS. FT-IR-EMS is indicated to have advantage over FT-IR-RAS in nonflat or rough-surfaced samples such as wires and steel tire cords. The semiquantitative analysis of thin layers is also possible with the technique.

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Fourier Transform Infrared Spectroscopy as a Powerful Tool for the Study of Carbohydrates in Aqueous Solutions

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FT-IR spectral investigations on carbohydrates were undertaken in aqueous media in order to facilitate the assignments of vibrational bands. For pure anomeric forms of glucose, FT-IR spectra obtained as a function of time revealed many changes in spectral content, providing new information about anomer characteristic bands in aqueous media. It was also found that fructose, which is known to undergo complex mutarotation, exhibits two types of spectral changes, whereas glucose, which undergoes simple mutarotation, shows a single type of spectral change. Thus FT-IR spectral investigations in aqueous carbohydrates should be able to distinguish between simple and complex mutarotation cases. As a vibrational spectroscopic technique, the importance of FT-IR spectroscopy is further emphasized by showing that Raman spectroscopy is not sensitive enough to reveal the structural changes of carbohydrates in aqueous media.

Index Headings: Fourier transform infrared; Carbohydrates; Raman spectroscopy.

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INTRODUCTION

Infrared spectroscopy has been employed to investigate the structural details of carbohydrates since the beginning of this century.¹ The early studies have employed the samples either in KBr disc or mull form and provided information to identify the absorption bands characteristic of the anomeric configuration in the solid state. This early work is summarized in three different reviews.²⁻⁴ The infrared studies in aqueous carbohydrate solutions, however, have not been undertaken systematically, perhaps due to the belief that strong absorption of infrared radiation by water might not permit useful investigations. This problem is generally felt more seriously with dispersive infrared spectrometers than with Fourier transform infrared (FT-IR) spectrometers owing to less light throughput in the former. The availability of water-insoluble windows did attract⁵ infrared investigations in aqueous solutions, but the advantages